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OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MAR 10 1988

MEMORANDUMSUBJECT: Leaching Assessment for Harmony and Degradates for the  
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The Ground-Water Team has been asked to assess the leaching potential of Harmony (Methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-amino]carbonyl]amino]sulfonyl]-2-thiophencarboxylate) for the Registration Standard. This transmittal summarizes the Ground-Water Team's conclusions and recommendations for the Registration Standard, the history of the chemical within EAB and its environmental fate profile.

CONCLUSIONS

Harmony is a sulfonyl urea. The chemical and several of its degradates are expected to leach to shallow ground water as a result of normal agricultural use. Because of the low rates of application, 80-100 g ai/ha, the chemical and its degradates are expected to reach shallow ground water in very low levels, less than 1 ppb, initially. Data from field dissipation studies using radio-labelled material show evidence of Harmony and its degradates moving down the soil profile with time and rainfall to the deepest depths sampled, that is, to 12-14 inches, at less than 1 ppb in the soil. A greater concentration may be expected in the water percolating through the soil profile as Harmony and its degradates are readily leached.

Harmony is less persistent than its degradates; it is expected to degrade with time. However, over time, degradates may build up in the unsaturated and saturated zones as they are resistant to hydrolysis and soil metabolism. Therefore, with time, greater concentrations of the degradates of Harmony are expected in shallow ground water.

#### RECOMMENDATIONS

To address the leaching potential, the following points are suggested for inclusion into the Registration Standard if they have not already been included through past EAB reviews:

1. The toxicological levels for Harmony (Methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-amino]carbonyl]amino]sulfonyl]-2-thiophencarboxylate) should be established.
2. The toxicological levels of the three degradates expected to leach and persist should be established. They are: triazine amine (4-methoxy-6-methyl-1,3,5-triazin-2-amine), and 2-ester-3-sulfonamide, and Harmony acid (3-[[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophencarboxylic acid).
3. There are several other degradates expected to leach; however, whether these compounds are persistent is at this time unknown. In order to address this question, the following studies should be required in the Registration Standard: an Aerobic Soil Metabolism study using the triazine-labelled moiety; an Anaerobic Soil Metabolism study using the triazine-labelled moiety; a small-scale prospective study to track the levels of Harmony and its degradates percolating to ground water.
4. Currently, the low levels of use of Harmony necessitate the use of radio-labelled compounds for residue analyses in soil and water. The registrant needs to develop a method using cold materials capable of detecting sulfonyl ureas and their degradates at low levels (that is, 1 ppb or less) as these are the expected levels in ground water. They will need such a method for detections of the sulfonyl ureas and degradates in ground water under actual use conditions. Otherwise, requiring any ground-water monitoring studies will be useless.
5. Finally, Harmony is but one of several sulfonyl ureas expected to have similar persistence and mobility characteristics. The Ground-Water Team recommends establishing the toxicological levels for all of these compounds and their triazine, thiophene, and acid degradates. Ground-water monitoring studies, either prospective or retrospective, should be considered in the future. These study requirements will have to be discussed in detail for each of the sulfonyl ureas currently registered in their respective Registration Standards or at some other time. This

serves as notification that EAB considers the sulfonyl ureas to have leaching potential as a class of compounds.

#### ENVIRONMENTAL FATE

**Hydrolysis:** Harmony degrades to triazine amine and 2-ester-3-sulfonamide at acidic pHs. Harmony showed resistance to hydrolysis at alkaline and neutral pHs. The triazine amine is resistant to hydrolysis. At pH 5 the parent degrades with a half-life of 3-6 days.

**Photolysis:** Harmony degrades under exposure to natural sunlight. Several degradates were identified: triazine amine and triazine urea, and a proposed, but unverified, photoproduct were the major degradates in water. The half-life for Harmony in water when exposed to natural sunlight varied with pH, but ranged from 1-6 days. In soil, the major degradates of Harmony were: triazine amine, 2-ester-3-sulfonamide, lesser degradates were triazine urea and the parent acid. Photolysis increases the degradation rate of Harmony. The half-life of Harmony on irradiated soil was 7-14 days, and 14-21 days in the dark controls. Photolysis in water and on soil is an important degradative pathway for the parent compound Harmony.

**Aerobic Soil Metabolism:** Harmony degrades under aerobic soil conditions to several compounds. They are: triazine amine, triazine urea, parent acid, and 2-ester-3-sulfonamide. Thiophene labelling allowed tracking of the formation and decline of the parent acid and 2-ester-3-sulfonamide degradates. Under aerobic conditions, the 2-ester-3-sulfonamide and the parent acid degradates increased and decreased over time. The parent acid degradate increased to a maximum concentration at 3 weeks and decreased to 6-18% of the original application at 20 weeks. The sulfonamide degradate reached a maximum concentration at 2 weeks and degraded to 0.5-0.8% of the original application at 20 weeks. Because the triazine moiety was not labelled in this study, the patterns of formation and decline of triazine amine and triazine urea could not be traced. However, from studies on chlorsulfuron, the triazine amine moiety is known to be persistent in aerobic soil systems. The half-life for Harmony is 2-6 days.

**Anaerobic Soil Metabolism:** Harmony degrades under anaerobic conditions to 2-ester-3-sulfonamide and variants of this thiophene compound. Triazine amine or urea are expected degradates, but this could not be verified as the parent compound was radio-labelled on the thiophene ring only, not the triazine ring and thiophene rings, both. Under anaerobic conditions, the thiophene degradates are moderately persistent. The parent compound has a half-life of 7-28 days depending on the soil type and soil pH. The more acidic the soil the more rapid the degradation of Harmony as acidic hydrolysis reactions and microbial degradation occur together. In a more basic soil, only microbial degradation occurs.

**Mobility:** Triazine and thiophene-labelled Harmony was added to soil columns and leached under worst-case conditions. The parent compound and the parent acid leached; 72-97% of the parent compound added to the columns leached as intact parent compound or the parent acid (exact percentages of each were not determined). Triazine and thiophene-labelled Harmony was aged for 6 days in soils and added to soil columns for leaching. The leachate contained triazine-labelled and thiophene-labelled residues, 69% and 72% of the originally applied material, respectively. The exact identity of the labelled residues was not determined. They were probably triazine amine, 2-ester-3-sulfonamide, and the parent acid, the major degradates from aerobic soil metabolism.

Laboratory batch equilibrium studies were used to determine the adsorption/desorption coefficients for Harmony and its acid. The Freundlich  $K_d$  values ranged from 0.08-1.38 for a mixture of the parent and acid in equilibrium solutions for four soils; two sand loams, one silt loam, and a silt. The desorption coefficients were 0.27-1.67 indicating weak and reversible sorption. There were no adsorption coefficients for the triazine amine.

**Field Dissipation:** Thiophene-labelled Harmony, and thiophene-labelled residues (2-ester-3-sulfonamide and parent acid) were shown to leach to 9-14 inches in the field at levels less than 1 ppb. The residues moved over time with rainfall downward. Studies with chlorsulfuron have shown the triazine-labelled moiety to leach to 12 inches in the field. The same behavior is expected of the triazine moiety from Harmony. The leaching depth of Harmony and its degradates was not defined by these studies. These studies were conducted on four soil types, none would be considered worst-case. Therefore, more leaching would be expected in very coarse, sandy soils.

#### HISTORY

EAB reviewers have outlined the fate and leaching potential of Harmony since 1984. In the most recent review on Harmony, dated April 10, 1987, the leaching potential of Harmony was clearly stated with deferral to the Toxicology Branch to determine whether Harmony or its degradates were of toxicological significance at the low ppb levels. This review concurs with this conclusion as stated previously in the Conclusion section of this memorandum.

cc: Paul Mastradone

AttachmentGlossary of terms

1. RfD, Reference Dose: Maximum exposure rate to a contaminant which results in an insignificant lifetime risk. Units are mg/kg/day to allow extrapolation from test animals to humans.
2. MPI, Maximum Permissible Intake: The RfD for a 60 kg (other programs sometimes assume a 70 kg) human. Units: mg/day  
 $MPI = RfD \times 60kg$
3. DWEL, Drinking Water Equivalent Level: The level of contamination of drinking water which results in consumption of the RfD. Calculated by assuming a 70 kg adult consumes 2 liters of contaminated water per day.  
 $DWEL = RfD \times 60 \text{ kg} / 2 \text{ liters/day}$ ; also  $DWEL = MPI / 2 \text{ liters/day}$   
 Units of the DWEL are ppb or ug/liter.
4. MCLG, Maximum Contaminant Level Goal: Maximum exposure rate of a contaminant which can be contributed by drinking water and still result in an insignificant lifetime risk in combination with presumed exposure through food residues. Generally 20% of the DWEL, but zero for carcinogens.  
 $MCLG = DWEL \times 0.2$ ; also  $MCLG = MPI \times 0.2 / 2 \text{ liters} = MPI \times 0.1 / \text{liters}$ . Units: ppb or ug/liter.
5. MCL, Maximum Contaminant Level: upper limit of contamination permitted in public drinking water supplies. Set as close as possible to MCLG taking into consideration technological feasibility of detection and purification. Units: ppb or ug/liter.
6. lifetime HA (or HAL), lifetime Health Advisory: derived the same way as MCLG. Used on an advisory basis, as a threshold level for deeming drinking water "safe enough" for use over period approximating a lifetime. Units: ppb or ug/liter.
7. contamination level resulting in  $10^{-6}$  risk factor for humans: level of contamination associated with a one in one million chance of cancer. Calculated in lieu of an MCLG or lifetime HA for A and B carcinogens. Units: ppb or ug/liter.
8. GRGL, Groundwater Residue Guidance Level: MCLG or, if none exists 5 ppb in current Senate bill.

LOC =  $DWL \times 0.2 \times 0.5 \rightarrow S.F.$

~~(0.5)(0.5)~~

↓

std cont. from H<sub>2</sub>O

382-3478

Joe Arcos

NULETTA

382-3513

angela asaretha in OTS.

any info on mutagenic activity

-mike waters in RTF also - mutagenic

- 919-541-2537

.07-.08

Harmony Levels of Concern (LOC) for leachates in ground water. Based on the NOEL of 25 ppm from the rat chronic feeding/oncogenic study the LOC is 37.5 ppb based on the following calculation:

25ppm /20 conversion factor /100 safety factor = 0.0125 mg/kg  
bodyweight/day.

$$0.0125 \text{ mg/kg/day} \times 1000 \text{ ugm/mg} \times 60 \text{ kg person} = 750 \text{ ugm/day}$$
$$750 \text{ ug}/\text{day} / 2 \text{ liters}/\text{day} = 375 \text{ ug}/\text{liter} = 375 \text{ ppb}$$

375 ppb X 0.5 safety factor X 0.2 Standard constant for drinking water = 37.5 ppb = LOC.

ADI  $.0125 \text{ mg/kg/day} \times 60 \text{ kg} = .75 \text{ mg/day}$   
 $\downarrow$   
 in 2 l  
 each l. =  $.375 \text{ mg/l}$   
 $\downarrow$   
 $\text{ADL} = .375 \text{ ppm}$   
 $\downarrow$   
 $\text{ADL} = .08 \text{ ppm}$   
 $\downarrow$   
 $\text{ADL} = .04$   
 $\downarrow$   
 $40 \text{ ppb}$



13544



# R056298

**Chemical:** Thifensulfuron

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